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(54) Title: ORAL AND PERSONAL HYGIENE ARTICLES CONTAINING ACTIVE AGENTS BONDED TO THE SURFACE THEREOF

(57) Abstract

An article suitable for oral or personal hygiene use, such as a toothbrush, toothpick, dental floss, denture, razor, eye glasses, contact lens, hair brush or comb, and comprised of polymeric material, has one or more chemically or biologically active agent(s) bonded to the surface thereof.

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ORAL & PERSONAL HYGIENE ARTICLES CONTAINING ACTIVE AGENTS BONDED TO THE SURFACE THEREOF

SUMMARY OF THE INVENTION

This invention relates to articles suitable for oral and personal hygiene use and comprised of polymeric material wherein the articles have bonded to the surface thereof one or more chemically or biologically active agent(s). Some examples of suitable articles include eye glasses, contact lens, toothbrushes, tooth picks, dentures, dental floss, razors, hair brushes and combs. The polymeric material is selected from the group consisting of polyamides, polystyrenes, styrene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene copolymers, polyacrylates, polyesters and polypropylenes; preferably nylon and cellulose acetate propionate. The active agent preferably is a quaternary ammonium compound, such as 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride.

This invention also relates to a method for applying a coating of chemically or biologically active agent(s) to an oral or personal hygiene article comprised of polymeric material by (a) directly permanently bonding said active agent to the surface of said article, or (b) (1) contacting said articles with an acid, alkaline hydroxide or organic solvent and (2) subsequently permanently bonding said active agent(s) to the surface of said article.

The invention yields oral and personal hygiene articles which have anti-bacterial and/or anti-microbial coatings and/or coatings of active agents useful in retarding or preventing plaque, gingivitis, periodontitis, tooth and gum pain and diseases and infections of the skin, hair, scalp and eyes.

BACKGROUND OF THE INVENTION AND INFORMATION DISCLOSURE

Oral and personal hygiene articles, such as toothbrushes and dental floss and the like, are constantly being improved for more effective cleaning and other benefits. Some of the benefits include the delivery of active agents to the teeth and gums and disinfectant properties of the oral hygiene articles.

Because toothbrushes, hair brushes and combs, in particular, can be a haven for bacterial and/or microbial growth, it would be especially beneficial to provide a toothbrush or other oral and personal hygiene articles which inhibit or prevent the growth of bacteria and/or other microbes thereon. Thus, it is an object of this invention to provide oral and personal hygiene articles which have one or more active agents bonded to the surface thereof. It is a further object of this invention to provide oral and personal hygiene articles which possess permanent or long-lasting anti-bacterial and/or anti-microbial activity. It is another object of this invention to provide an easy and efficient method for applying a coating of active agent(s) to an oral or personal hygiene article by (a) directly permanently bonding the active agent(s) to the surface of the article or (b) by contacting it with an acid, alkaline base or organic solvent and subsequently permanently bonding the active agent(s) to the surface of the article.

Many references in the art describe antibacterial compositions and the use of these to treat various surfaces. US Patent No. 4,866,192 describes organosilicone quaternary ammonium antimicrobial compounds to treat rayon fabric and other surfaces. US Patent No. 4,371,577 describes antimicrobial carpet which has been treated with an amino acid type surfactant and an organosilicone quaternary ammonium salt. US Patent No. 4,621,120 describes antibacterial compositions comprising vinyl copolymers having quaternary nitrogen groups. These compositions are disclosed as being useful in mouthwashes, toothpastes and dental creams.

US Patent No. 3,170,901 describes quaternary ammonium compounds and polymers thereof which are useful in treating paper and textile fabrics for imparting

increase wet strength, water repellency, and resistance to shrinkage. US Patent No. 4,025,617 describes antimicrobial quaternary-ammonium copolymers formed by the condensation of at least two di-functional tertiary amines and 1,4-dihalo-2-butene. These copolymers are described as being useful for the antimicrobial treatment of circulatory and standing waters.

US Patent No. 4,482,680 discloses poly(vinylbenzyl quaternary ammonium) halides which are useful as preservatives for cosmetic and pharmaceutical compositions and as disinfectant cleansers. US Patent No. 4,161,518 describes dentifrice compositions containing a quaternary ammonium organosilicone. US Patent No. 4,394,378 describes certain silyl quaternary ammonium salts, such as 3-(trimethoxylsilyl) propyldidecylmethyl ammonium chloride, which is useful for antimicrobial treatment of textile fibers, siliceous materials, metals, leather, wood and plastics.

US Patent No. 4,161,518 describes dentifrice compositions containing a quaternary ammonium organosiloxane which is useful in inhibiting plaque formation on teeth. US Patent No. 4,615,937 describes antimicrobially-active web and wet wipes containing an organosilicone quaternary ammonium salt. US Patent No. 4,721,511 describes antimicrobial fabrics having a bioactive amount of a silicone quaternary amine. US Patent No. 4,282,366 describes natural and synthetic fabrics impregnated with organosilicone quaternary ammonium compounds as antimicrobial agents.

A method for preparing antimicrobial foams containing quaternary ammonium salts of silanes is described in US Patent No. 4,631,297. US Patent No. 4,408,996 describes a process for dying bioactive cellulosic fabrics by applying a mixture of organosilicone polymer, a dye and a silyl quaternary amine.

US Patent No. 3,730,701 describes a method for controlling the growth of algae in water by adding certain silyl quaternary amines. US Patent No. 4,847,088 describes synergistic antimicrobial compositions comprising a quaternary ammonium compound and an acid

which are useful in treating carpets, fabrics, walls and furnishings.

Articles, such as "Disinfection of Water with Quaternary Ammonium Salts Insolubilized on a Porous Glass Surface," Nakagawa et al, Applied and Environmental Microbiology, March 1984, p-513-518; and "Algicidal Activity of a Surface-Bonded Organosilicone Quaternary Ammonium Chloride," Walters et al, Applied Microbiology, Feb. 1973, P. 253-256 describe the antimicrobial activity of bound quaternary ammonium salts.

DETAILED DESCRIPTION

The present invention relates to personal and oral hygiene products which have been treated to bond active agent(s)to their surfaces. Specifically, the present invention involves an article comprised of polymeric material having bonded to the surface thereof one or more chemically or biologically active agent(s), wherein said article is suitable for oral or personal hygiene use, and said active agent is substantially non-leachable from the surface of said article in a water-based medium.

Articles covered by this invention include any article of manufacture which is suitable for oral or personal hygiene use. Oral hygiene as used herein means useful for cleaning and caring for the teeth, gums, dentures or any other parts of the oral cavity. Personal hygiene as used herein means useful for cleaning and caring for the hair, scalp, skin, ears, nose, eyes and other parts of the face and head. Preferred articles within the scope of this invention include a toothbrush, dental floss, toothpick, comb, hair brush, razor, eyeglass lens and frames and contact lens.

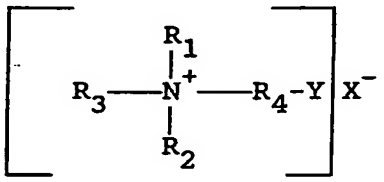
Suitable articles according to this invention may be composed partly or entirely of a polymeric material or have an exterior surface comprised of a polymeric material. The polymeric material can be a natural or synthetic polymer. The polymeric material preferably is polyamides, polyacrylates, polyesters, polypropylenes, polystyrenes, styrene-acryl-onitrile copolymers, acrylonitrile-butadien-

estyrene copolymers, cellulose esters and blends and combinations thereof. The most preferred polymeric materials are nylon and cellulose acetate propionate.

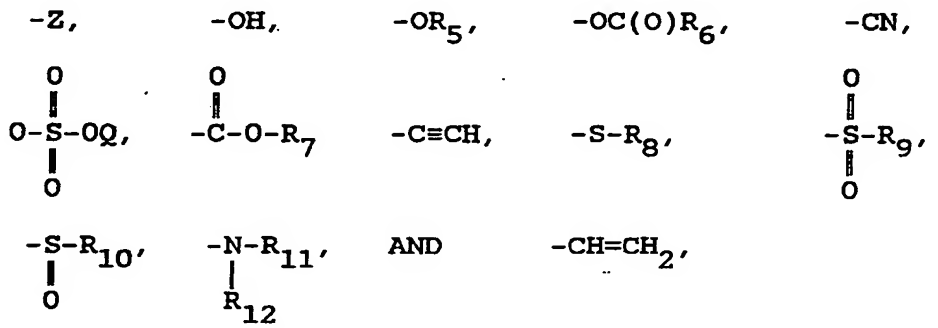
An essential feature of this invention is that the article has permanently bonded to the polymeric surface thereof one or more chemically or biologically active agent(s). These active agent(s) are bonded to the polymeric surfaces of the article, such that the agent(s) are substantially non-leachable from the surface of said article in a water-based medium. Suitable active agents

would include any compound(s) having antimicrobial activity and which are capable of being bonded to the polymeric surfaces of the article. Preferred active agents include the quaternary ammonium compounds, organosilicone quaternary ammonium compounds, cetyl pyridinium compounds, guanidine compounds, bis-guanidine compounds and isothiouronium halide compounds.

Preferred quaternary ammonium compounds useful for this invention have the formula:

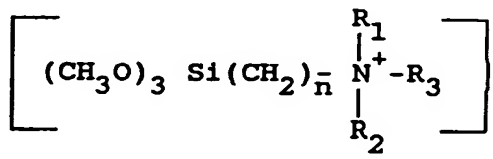


Wherein R_1 is CH_2-phenyl or an alkyl group containing about 8-22 carbon atoms; R_2 is methyl, ethyl or an alkyl group containing about 8-22 carbon atoms; R_3 is methyl or ethyl; R_4 is an alkyl group containing about 1-6 carbon atoms; X is an anion; and Y is a group having the structure:



wherein R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, are alkyl groups containing about 1-12 carbon atoms or phenyl; Z is halogen and Q is hydrogen or a cation.

The more preferred organosilicone quaternary ammonium compounds useful for this invention have the formula:



wherein R_1, R_2, and R_3 are as described above, X is an anion and n is an integer from about 1-6 (preferably 3-6).

The most preferred organosilicone quaternary ammonium compounds are n-octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, n-tetradecyldimethyl [3-(trimethoxysilyl) propyl] ammonium chloride, n-decyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, n-didodecylmethyl[3-(trimethoxysilyl)propyl] ammonium chloride, and n-dodecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride.

Other active agents can include the nitrogen as part of a heterocyclic system, such as a cetyl pyridinium compound. The preferred cetyl pyridinium compound is 2-(3-trimethoxysilylpropyl)-N-cetyl pyridinium bromide.

The isothiouronium halide compounds are also suitable for use as active agents according to this invention. The preferred isothiouronium halide compound for use in this invention is (trimethoxysilylpropyl) isothiouronium chloride.

The articles of this invention have the active agent(s) bonded to the polymeric surfaces of the

articles, such that the active agent(s) is permanently attached to the articles. To be suitable for oral and personal hygiene use, the articles must have the active agent(s) bonded to the polymeric surfaces thereof such that the agent(s) is substantially non-leachable in an aqueous medium. Thus, the articles have a polymeric surface which has permanent antibacterial and/or antimicrobial activity which can not be leached out by saliva, shampoos, shaving creams, toothpastes and other aqueous-containing mediums.

The active agents can be permanently attached to the polymeric surfaces of the articles by any suitable means, such as chemical linking using multifunctional reactive organics (such as bis-carbenes or bis-nitrenes), silane coupling systems, plasma activation, flame activation, chemical treatment and other polymer grafting techniques.

The preferred attachment mechanism is a silane coupling system. It is believed, although Applicant does not intend to be limited thereby, that the alkoxysilyl end of the active agent is hydrolyzed to the corresponding hydroxy component in the presence of water. This component then reacts with the active -OH, amide or other reactive sites on the polymeric material. Although the active agent can be bonded to the polymeric surface of the article by any type of bonding, it is preferred that the agent be covalently bonded to the polymeric surface of the article.

The present invention also includes a method for applying a coating of chemically or biologically active agent to an oral or personal hygiene article comprised of polymeric material. This method can involve permanently

bonding the active agent directly to the untreated surface of the article. The method can also comprise the steps of:

1. contacting said article with a solvent selected from the group consisting of an aqueous-based organic or inorganic acid, an aqueous-based alkaline hydroxide or an organic solvent, and
2. subsequently bonding said active agent to the surface of said article.

The invention also includes articles which have been treated by the above methods.

It is believed, although Applicant does not intend to be bound or limited hereby, that treating the polymeric surface of the article with the solvent exposes or forms reactive sites on the polymeric surface to which the active agents can bond. Preferably, the polymeric surface of the article has greater than about 2% of the surface area containing active sites for bonding of the active agent; more preferably greater than about 5%.

Thus, suitable solvents for treating the polymeric surfaces of the article include any material which would expose or form reactive -OH, amide, or other reactive sites on the polymeric surfaces for bonding of the active agents. Some examples of suitable solvents include aqueous-based organic and inorganic acids, aqueous-based alkaline hydroxides and organic solvents. The preferred acids are sulfuric and acetic acid. The preferred alkaline hydroxides are potassium hydroxide and sodium hydroxide. Preferred organic solvents include methanol, ethanol, isopropanol, acetone and ethyl acetate.

The polymeric surfaces of the articles are contacted with the solvent for a sufficient time ranging anywhere from a few minutes to several hours. The solvents can be used alone, in combination or sequentially.

In bonding the active agent to the polymeric surface of the article, the article can be contacted with the active agent for a sufficient time for the active agent to bond to the surface. Preferably, the active agent is in a solution of water or other suitable solvent. The solution can contain the active agent in any concentration, but preferably contains from about 1% to about 4% wt./vol. of the active agent. After contacting the article with the solution of active agent for a sufficient period of time (preferably about 30 minutes or longer), the article can be dried, rinsed and cured at an elevated temperature (preferably about 50-125°C). The drying and curing conditions, such as temperature, time and humidity, should be selected such that the dimensional stability of the article is not adversely affected.

The articles of this invention are effective against a wide variety of microbial species, and they continuously inhibit the growth of microbial organisms on the surface thereof. The articles have demonstrated antimicrobial activity against Candida albicans, Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli, Streptococcus mutans/faecalis and Klebsiella pneumoniae.

The following examples are presented to help demonstrate the present invention. The examples are intended to be illustrative and not in a limitative

sense. This invention includes the embodiments described and exemplified herein and all equivalents thereof. All parts and percentages used in the examples are on a weight basis unless otherwise indicated.

EXAMPLE I

Various treatment solutions were prepared within the scope of this invention containing 1%, 2% and 4% wt./vol., respectively, of the active agent. Each solution was prepared by mixing 10 ml. of concentrated acetic acid and 2 grams of surfactant (Zonyl FSN from DuPont Co.) with deionized water, followed by either 10, 20 or 40 grams of the active agent, to make one liter of each solution. The solution is agitated for about 30 minutes to hydrolyze the active agent.

These solutions are presented in Table I below:

TABLE I

Solution	Active Agent	Amt. (Wt./Vol.)
Sample 1	n-octadecyldimethyl [3-(trimethoxy-silyl)propyl] ammonium chloride	1%
Sample 2	"	2%
Sample 3	"	4%
Sample 4	n-tetradecyldimethyl]3-trimethoxy-silyl)propyl] ammonium chloride	1%
Sample 5	"	2%
Sample 6	"	4%
Sample 7	(trimethoxysilylpropyl) isothiouronium chloride	1%
Sample 8	"	2%
Sample 9	"	4%
Sample 10	2-(3-trimethoxysilylpropyl)-N-cetyl pyridinium bromide	1%
Sample 11	"	2%
Sample 12	"	4%

EXAMPLE II

Nylon toothbrush bristle fibers were treated with the solutions of samples 1-3 by agitating the bristles in the respective solutions for about 30 minutes. The bristle fibers were removed from the solutions and dried at ambient conditions for about 3 hours. The fibers were then rinsed with deionized water and heated in an oven for about 10 minutes at about 125°C. The fibers were cooled at room temperature and the samples were place in inocula of Staphylococcus aureus, Pseudomonas aeruginosa and Candida albicans, respectively. The fibers were then removed from the inocula. One sample from each inoculum was placed immediately in Letheen Broth, agitated, and a sample of the broth was then plated onto plate count agar via spiral plater. The numbers of colony forming units per milliliter were measured. Other samples from each inoculum were allowed to dry for 1 hour or 23 hours before being placed in the Letheen Broth as described above. Bristle fibers not treated with the active agent solutions were used as a control and evaluated in tandem with the treated bristles. The results are presented in Table II below.

TABLE II

SAMPLE	INITIAL*	1 HOUR*	% CHANGE	23 HOUR*	% CHANGE
Microorganism: Staphylococcus aureus					
CONTROL	2.7×10^5	2.1×10^5	-22.2	3.7×10^5	+37.0
SAMPLE 3	2.4×10^5	2.2×10^5	-8.3	7.1×10^3	-97.0
SAMPLE 2	1.8×10^5	1.4×10^5	-22.2	1.2×10^4	-93.3
SAMPLE 1	3.3×10^5	2.6×10^5	-21.2	6.5×10^4	-80.3
Microorganism: Pseudomonas aeruginosa					
CONTROL	8.0×10^5	4.6×10^5	-42.5	1.9×10^3	-99.8
SAMPLE 3	5.5×10^5	3.1×10^5	-43.6	7.1×10^1	-99.9
SAMPLE 2	3.6×10^5	3.3×10^5	-8.3	5.4×10^0	-99.9
SAMPLE 1	4.9×10^5	4.7×10^5	-4.1	1.85×10^2	-99.9
Microorganism: Candida albicans					
CONTROL	3.9×10^4	3.9×10^4	0	2.1×10^3	-94.6
SAMPLE 3	3.9×10^4	4.1×10^4	+5.1	9.8×10^1	-99.8
SAMPLE 2	5.9×10^4	6.5×10^4	+10.2	8.7×10^2	-98.5
SAMPLE 1	4.2×10^4	3.2×10^4	-23.8	3.1×10^3	-92.6

* (Colony forming units per ml.)

EXAMPLE III

Following the procedures of Example II, toothbrush heads comprised of cellulose acetate propionate were treated with the solutions of Samples 1-3 and evaluated for antimicrobial activity. The results are presented in Table III below.

TABLE III

SAMPLE	INITIAL*	1 HOUR*	% CHANGE	23 HOUR*	% CHANGE
Microorganism: Staphylococcus aureas					
CONTROL 1	2.0×10^6	1.6×10^6	-20.0	1.9×10^6	-5.0
CONTROL 2	2.0×10^6	1.6×10^6	-20.0	1.8×10^6	-10.0
SAMPLE 3	2.0×10^6	5.7×10^5	-71.5	8.7×10^2	-99.9
SAMPLE 2	2.0×10^6	6.7×10^5	-66.5	1.5×10^2	-99.9
SAMPLE 1	2.0×10^6	5.5×10^5	-72.5	2.0×10^2	-99.9
Microorganism: Pseudomonas aeruginosa					
CONTROL 1	1.7×10^6	1.2×10^6	-29.4	6.0×10^5	-64.7
CONTROL 2	1.7×10^6	1.1×10^6	-35.3	3.8×10^5	-77.7
SAMPLE 3	1.6×10^6	1.2×10^6	-25.0	1.4×10^5	-91.3
SAMPLE 2	1.7×10^6	1.2×10^6	-29.4	5.0×10^4	-97.1
SAMPLE 1	1.7×10^6	1.2×10^6	-29.4	3.2×10^5	-81.2
Microorganism: Candida albicans					
CONTROL 1	2.0×10^5	6.0×10^4	-70.0	7.8×10^5	+290.0
CONTROL 2	1.9×10^5	6.4×10^4	-66.3	4.3×10^5	+126.3
SAMPLE 3	2.4×10^5	5.1×10^4	-78.8	1.5×10^3	-99.4
SAMPLE 2	1.6×10^5	3.4×10^4	-78.8	1.6×10^1	-99.9
SAMPLE 1	1.7×10^5	5.5×10^4	-67.7	2.4×10^2	-99.9

* (Colony forming units per ml.)

EXAMPLE IV

Following the procedures of Example II, toothbrush heads comprised of cellulose acetate propionate were treated with the solutions of samples 4-6 and evaluated for antimicrobial activity. The results are present in Table IV below.

TABLE IV

SAMPLE	INITIAL*	1 HOUR*	% CHANGE	23 HOUR*	% CHANGE
Microorganism: Staphylococcus aureas					
CONTROL	5.1×10^5	7.5×10^5	+47.1	4.9×10^5	-3.9
SAMPLE 6	4.2×10^5	8.8×10^4	-79.1	1.5×10^2	-99.9
SAMPLE 5	5.4×10^5	3.5×10^5	-35.2	1.8×10^5	-66.7
SAMPLE 4	3.3×10^5	2.9×10^5	-12.1	1.1×10^3	-99.7
Microorganism: Pseudomonas aeruginosa					
CONTROL	7.9×10^5	5.9×10^5	-25.3	1.8×10^2	-99.9
SAMPLE 6	7.5×10^5	6.1×10^5	-18.7	6.4×10^2	-99.9
SAMPLE 5	7.9×10^5	6.9×10^5	-12.7	1.8×10^3	-99.8
SAMPLE 4	8.0×10^5	6.6×10^5	-17.5	1.6×10^2	-99.9
Microorganism: Candida albicans					
CONTROL	5.5×10^3	5.5×10^3	0	1.1×10^2	-98.0
SAMPLE 6	1.1×10^4	6.7×10^3	-39.1	0	-100.0
SAMPLE 5	1.5×10^4	9.5×10^3	-36.7	7.1×10^1	-99.5
SAMPLE 4	8.5×10^3	5.7×10^3	-32.9	0	-100.0

* (Colony forming units per ml.)

EXAMPLE V

Following the procedures of Example II, toothbrush heads comprised of cellulose acetate propionate were treated with the solutions of Samples 7-9 and evaluated for antimicrobial activity. The results are presented in Table V below.

TABLE V

SAMPLE	INITIAL*	1 HOUR*	% CHANGE	23 HOUR*	% CHANGE
Microorganism: Staphylococcus aureas					
CONTROL	5.7×10^5	4.9×10^5	-13.6	1.2×10^6	+102.4
SAMPLE 9	5.7×10^5	4.0×10^4	-93.0	5.2×10^3	-99.1
SAMPLE 8	6.6×10^5	1.8×10^4	-97.3	1.9×10^4	-97.1
SAMPLE 7	6.9×10^5	4.8×10^5	-99.3	9.8×10^5	+41.0
Microorganism: Pseudomonas aeruginosa					
CONTROL	2.1×10^6	2.2×10^6	+5.3	2.3×10^5	-88.7
SAMPLE 9	2.2×10^6	2.1×10^6	-3.2	4.4×10^1	-99.9
SAMPLE 8	2.2×10^6	2.1×10^6	-5.5	7.3×10^4	-96.6
SAMPLE 7	2.2×10^6	2.2×10^6	0	3.8×10^3	-99.8
Microorganism: Candida albicans					
CONTROL	1.4×10^4	6.4×10^3	-54.5	2.1×10^3	-85.1
SAMPLE 9	6.3×10^3	4.6×10^2	-92.7	1.1×10^1	-99.8
SAMPLE 8	1.5×10^4	2.0×10^3	-86.5	1.1×10^3	-92.7
SAMPLE 7	2.4×10^4	7.1×10^4	+195.4	3.3×10^4	+37.9

* (Colony forming units per ml.) f

EXAMPLE VI

Following the procedures of Example III, toothbrush heads comprised of cellulose acetate propionate were treated with the solutions of Samples 10-12 and evaluated for antimicrobial activity. The results are presented in Table VI below.

TABLE VI

SAMPLE	INITIAL*	1 HOUR*	% CHANGE	23 HOUR*	% CHANGE
Microorganism: Staphylococcus aureas					
CONTROL	2.9×10^5	2.0×10^5	-31.0	2.2×10^5	-24.1
SAMPLE 12	2.7×10^5	1.4×10^5	-48.1	1.7×10^4	-93.7
SAMPLE 11	3.1×10^5	2.1×10^5	-32.3	2.0×10^4	-93.6
SAMPLE 10	3.2×10^5	2.4×10^5	-25.0	4.8×10^4	-85.0
Microorganism: Pseudomonas aeruginosa					
CONTROL	6.7×10^5	6.4×10^5	-4.5	2.7×10^3	-99.6
SAMPLE 12	6.8×10^5	6.9×10^5	+1.5	3.9×10^2	-99.9
SAMPLE 11	6.0×10^5	4.5×10^5	-25.0	7.1×10^3	-99.9
SAMPLE 10	8.7×10^5	6.7×10^5	-23.0	2.1×10^3	-99.8
Microorganism: Candida albicans					
CONTROL	3.5×10^4	3.1×10^4	-11.4	1.4×10^2	-99.6
SAMPLE 12	4.4×10^4	2.5×10^4	-43.2	2.9×10^2	-99.3
SAMPLE 11	3.3×10^4	3.2×10^4	-3.0	6.0×10^2	-98.2
SAMPLE 10	4.0×10^4	3.4×10^4	-15.0	9.7×10^2	-99.6

* (Colony forming units per ml.)

EXAMPLE VII

Toothbrush heads comprised of cellulose acetate propionate, and treated with the solution of Sample 3 according to the procedures of Example II, were evaluated for leachability of the active agent. Some of these treated toothbrush heads were washed several times with water, while others were unwashed.

The washed and unwashed toothbrush heads were evaluated for leachability using a bromophenol blue colorimetric analytical method. A bromophenol blue solution was prepared by mixing 0.1125 grams bromophenol blue, 450 grams of deionized water and 0.75 ml. of 10% Na_2CO_3. Two of the washed toothbrush heads were placed in a 4-ounce french square bottle along with 50 ml. of the bromophenol blue solution and 2 ml. of 2% Triton X-100 wetting agent. Two of the unwashed toothbrush heads were also placed in a similar bottle with 50 ml. of the bromophenol blue solution and Triton wetting agent. The bottles were shaken for about 20 minutes and allowed to sit. After periods of 1-hour, 12-hours and 24-hours, solution from each bottle was poured into cuvets and the transmittance measured on a spectrophotometer at 589 nanometers.

In the procedure, the blue dye reacts with the bound active agent on the toothbrush heads, causing a decrease in the bromophenol blue solution's color intensity. This loss of color intensity is a quantitative measure of the amount of active agent bonded to the surface of the toothbrush heads.

The results of the evaluation are presented in Table VII below.

Sample	(Absorbance Units) Sampling Time in Hours (0)	(1)	(12)	(24)
A. Washed Toothbrush Heads	0.32	0.30	0.31	0.33
B. Unwashed Toothbrush Heads	0.31	0.30	0.33	0.33
C. Bromophenol Blue Solution Control	0.53	0.53	0.53	0.53

(sample to sample variation is less than ± 0.02 absorbance units)

The above results show no significant difference between the washed and unwashed toothbrush heads, indicating no leaching of the active agent initially or over time.

CLAIMS

1. An article comprised of polymeric material having bonded to the surface thereof one or more chemically or biologically active agent, wherein said article is suitable for oral or personal hygiene use, and said active agent is substantially non-leachable from the surface of said article by a water-based medium.

2. The article of Claim 1 wherein said polymeric material is selected from the group consisting of polyamides, polyacrylates, polyesters, polypropylenes, cellulose esters, polystyrenes, styrene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene copolymers and mixtures thereof.

3. The article of Claim 2 wherein said polymeric material is nylon.

4. The article of claim 2 wherein said polymeric material is cellulose acetate propionate.

5. The article of claim 1 wherein said active agent is covalently bonded to the polymeric surface thereof.

6. The article of claim 1 where said article is a toothbrush.

7. The article of claim 1 wherein said article is dental floss.

8. The article of claim 1 wherein said article is a toothpick.

9. The article of claim 1 wherein said article is a comb.

10. The article of claim 1 wherein said article is a hair brush.

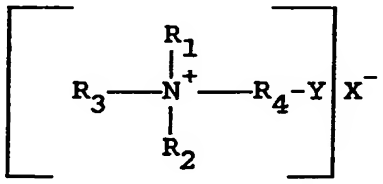
11. The article of claim 1 wherein said article is a razor.

12. The article of claim 1 wherein said article is a contact lens.

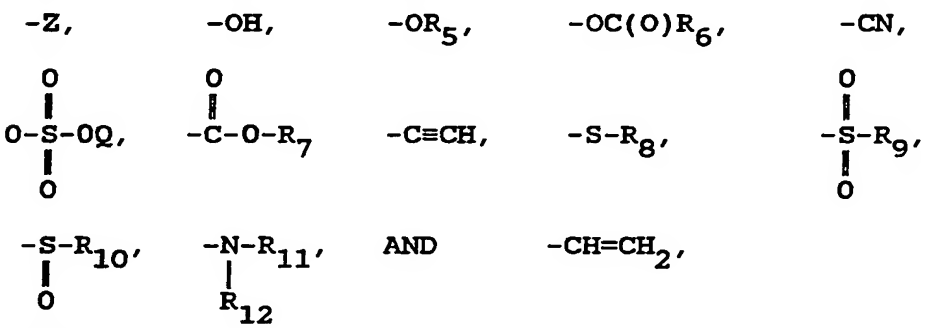
13. The article of claim 1 wherein said article is eye glasses.

14. The article of claim 1 wherein said active agent is a quaternary ammonium compound.

15. The article of claim 14 wherein said active agent is a quaternary ammonium compound having the formula:



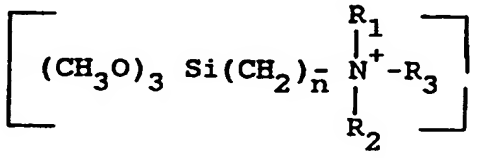
wherein R_1 is CH_2-phenyl or an alkyl group containing about 8-22 carbon atoms; R_2 is methyl, ethyl or an alkyl group containing about 8-22 carbon atoms; R_3 is methyl or ethyl; R_4 is an alkyl group containing about 1-6 carbon atoms; X is an anion; and Y is a group having the structure:



wherein R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12} are alkyl groups containing about 1-12 carbon atoms or phenyl; Z is halogen and Q is hydrogen or a cation.

16. The article of claim 1 wherein said active agent is an organosilicone quaternary ammonium compound.

17. The article of claim 16 wherein said organosilicone quaternary ammonium compound has the formula:



wherein R_1 is $-CH_2$-phenyl or an alkyl group having from about 8-22 carbon atoms, R_2 is a methyl, ethyl or an alkyl group containing about 8-22 carbon atoms, R_3 is methyl or ethyl, X is an anion and n is an integer from about 1-6.

18. The article of claim 16 wherein said organosilicone quaternary ammonium compound is n-octadecyldimethyl [3-(trimethoxysilyl)propyl] ammonium chloride

19. The article of claim 16 wherein said organosilicone quaternary ammonium compound is n-tetradecyldimethyl [3-(trimethoxysilyl) propyl] ammonium chloride.

20. The article of claim 1 wherein said active agent is (trimethoxysilylpropyl) isothiouronium chloride.

21. The article of claim 1 wherein said active agent is 2-(3-trimethoxysilylpropyl)-N-cetyl pyridinium bromide. 22. The article of claim 1 wherein said polymeric material is treated by contact with a solvent selected from the group consisting of an aqueous-based organic or inorganic acid, an aqueous-based alkaline hydroxide and an organic solvent, and subsequently said active agent is bonded to the surface of said treated polymeric material.

23. The article of claim 22 wherein said acid is selected from the group consisting of sulfuric acid and acetic acid.

24. The article of claim 22 wherein said alkaline hydroxide is selected from the group consisting of potassium hydroxide and sodium hydroxide.

25. The article of claim 22 wherein said organic solvent is selected from the group consisting of methanol, ethanol, isopropanol, acetone and ethyl acetate.

26. The article of claim 22 wherein said active agent is selected from the group consisting of n-octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, n-tetradecyldimethyl [3-(trimethoxysilyl) propyl] ammonium chloride, 2-(3-trimethoxysilylpropyl)-N-cetyl pyridinium bromide, and (trimethoxysilylpropyl) isothiouronium chloride.

27. A method for applying a coating of chemically or biologically active agent to an oral or personal hygiene article comprised of polymeric material comprising permanently bonding said active agent to the surface of said article.

28. The method of claim 27 comprising the steps of:
1) contacting said article with a solvent selected from the group consisting of an aqueous-based organic or inorganic acid, an aqueous-based alkaline hydroxide and an organic solvent; and
2) subsequently bonding said active agent to the surface of said article.

29. The method of claim 27 wherein said article is selected from the group consisting of toothbrushes, toothpicks, dental floss, dentures, hair combs, hair brushes, razors, eye glasses and contact lens.

30. The method of claim 27 where said polymeric material is nylon.

31. The method of claim 27 wherein said polymeric material is cellulose acetate propionate.

32. The method of claim 27 wherein said active agent is selected from the group consisting of n-octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, n-tetradecyldimethyl [3-(trimethoxysilyl) propyl] ammonium chloride, n-dodecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, n-didodecylmethyl [3-(trimethoxysilyl)propyl] ammonium chloride, 2-(3-trimethoxysilylpropyl)-N-cetyl pyridinium bromide, and (trimethoxysilylpropyl) isothiouronium chloride.

33. The method of claim 28 wherein said solvent is selected from the group consisting of sulfuric acid, acetic acid, potassium hydroxide, sodium hydroxide, methanol, ethanol, isopropanol, acetone and ethyl acetate.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/09116

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A01N25/34; A01N55/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	APPLIED MICROBIOLOGY vol. 24, no. 6, December 1972, US pages 859 - 863; A. J. ISQUITH ET AL: 'Surface-Bonded Antimicrobial Activity of an Organosilicon Quarternary Ammonium Chloride' see the whole document	1,2,4,5, 14, 16-18, 22,25,26
Y		6-11, 27-33
X	EP,A,0 355 765 (DOW CORNING) 28 February 1990 see page 2, line 15 - line 23 see page 3, line 41 - line 58 see page 4, line 19 - line 25 see page 4, line 42 - page 5, line 53	1-3,5, 14, 16-19, 21,27, 30,32

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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
05 JUNE 1992	23.06.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	W. Lamers

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PCT/US 91/09116

International Application No

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	WO,A,8 701 400 (JAMES RIVER CORPORATION) 12 March 1987 see page 1, paragraph 1 see page 3, paragraph 3 see page 4, paragraph 2 see page 5, paragraph 3 see page 7, paragraph 2 see page 9, paragraph 2 & US,A,4 615 937 7 October 1986 cited in the application	1,2,4,5, 14, 16-19, 27,31
X	US,A,2 938 814 (S. I. COHEN ET AL.) 31 May 1960 see the whole document	1-3, 5-11,27, 29,30
Y	EP,A,0 413 833 (SUNSTAR KABUSHIKI KAISHA) 27 February 1991 see page 3, line 3 - line 4 see page 3, line 52 - page 4, line 30 see claim 1	6-11, 27-33
X	WO,A,8 904 330 (IOPTEX RESEARCH) 18 May 1989 see page 1, paragraph 1 see page 3, paragraph 3 - page 5, paragraph 1 see page 9, paragraph 2 - page 17 see page 24, paragraph 2 see claims 1,11,28,37	1,2,5, 12,13
Y		29
Y	US,A,4 472 327 (C. W. NEEFE) 18 September 1984 see the whole document	29
X	GB,A,2 045 055 (DOW CORNING) 29 October 1980 see page 1, line 7 - line 20	1,20
X	FR,A,1 274 388 (E.I. DU PONT DE NEMOURS) 18 September 1961 see page 1 see page 3; example 4 see page 5; examples 6-14 see claims 1-7	1-3,5, 14,15
X	US,A,4 035 146 (M. W. BRENNER ET AL.) 12 July 1977 see column 1, line 7 - line 10 see column 2, line 27 - column 3, line 55 see column 4, line 1 - line 21	1,2,4, 14,15, 22-24

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International Application No PCT/US 91/09116

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 296 441 (HENKEL) 28 December 1988 see page 2, line 16 - line 23 see page 2, line 37 - line 42 see page 3, line 19 - line 28 see page 3, line 44 - page 4, line 10 see page 4, line 48 - line 54 see claims 1,3,5 ---	1,2,14, 15

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